

# THE MEASUREMENT OF PHASE EQUILIBRIA FOR PROCESS STREAMS AT OPERATING TEMPERATURES AND THE IMPLICATIONS FOR THE CRE LIQUEFACTION PROJECT

A Waller, S T Walton  
CRE  
Point of Ayr Facility  
Ffynnongroew  
Clwyd UK  
CH8 9JJ

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## INTRODUCTION

CRE operates the Liquid Solvent Extraction process at its pilot plant in North Wales, UK. The process involves feeding pulverised coal, slurried with a solvent, to a digester in which much of the coal is dissolved. Filtration removes residual solids. The coal solution is fed to an ebulliating bed hydrocracker, together with hydrogen at 200 bar at 425°C. The catalytic reaction adds hydrogen to the coal solution which is distilled to recover solvent and yield a product.

The vessels and pipework are externally heated to ensure that liquids can be pumped but temperatures are not high enough to initiate regressive reactions with consequent formation of carbonaceous solids. However, coal derived liquids are complex mixtures of hydrocarbons which are not soluble in all proportions at all temperatures. Precipitation may occur, leading to blockages in process lines and equipment with subsequent interruption to plant operation. Coal liquids can be regarded simply as a three component system comprising pitch (material with a boiling point >450°C), saturated hydrocarbon (saturates) having a boiling point <450°C and distillate solvent, the remainder of the material boiling below 450°C.

Coal solution, of which LSE recycle solvent is a particular case, is a mixture of these three components. A study was undertaken to examine the quantity and nature of precipitates formed from coal solutions of various compositions, with a view to preventing plant shutdowns caused by blocked lines.

## METHOD

Coal solutions and a coal derived wash oil were selected from appropriate process streams and analysed to determine their pitch and saturates content. The solutions were combined to prepare liquids of varying proportions of distillate solvent, pitch and saturates. The liquid was filtered on a laboratory scale filter rig. (Figure 1) to determine the quantity of precipitate formed.

Coal solution was added to the electrically heated reservoir and allowed to reach a temperature of 200°C. Wash oil was added slowly with stirring to ensure that the temperature of the liquid in the reservoir did not change. Any light material flashing off was collected in a cold trap and returned to the liquid. A 1 bar nitrogen over pressure was applied.

The electrically heated filter body was fitted with a glass fibre filter and allowed to reach 200°C.

On opening the valve the liquid was allowed to pass through the filter paper and the mass of filtrate collected per unit time was recorded. On completion the filter body was dismantled and the mass of precipitate recorded and expressed as a percentage of the total mass of liquid added to the reservoir.

## RESULTS

The results were plotted on a triangular co-ordinate system to illustrate a family of curves. Each axis represents one of the three components of the system, distillate solvent, pitch and saturates. Each curve connects points of approximately equal amounts of precipitate (Table 1, Figure 2).

An important property of a triangular diagram is the significance of a straight line joining an apex to a point on the opposite edge. Movement along this line represent a change in the composition of one component while the other two components remain in the same proportions. Therefore as one component is added to the system, the composition of the mixture will always lie at some point on the line.

Figure 3 shows such a system. Lines AA', BB' and CC' drawn from the pitch apex to the opposite base line represents the case where pitch is added to an initial binary mix of distillate solvent and saturates with an initial composition of 80:20, 90:10 and 95:5 respectively. The lines show that as pitch levels increase the quantity of precipitate produced increases to a maximum at approximately 20% pitch and then decreases. The highest level of precipitated material occurs with the highest level of saturates in the mixture.

A typical coal solution will contain slightly more than 40% pitch and a typical LSE solvent some 30% pitch. Figure 3 illustrates the effect of increasing saturates in a typical coal solution (EE') and a solvent (DD').

Within the operating envelope of the plant then as the saturates levels increase the quantity of precipitate produced will continue to increase i.e. up to a saturates level of some 20%.

The nature of the precipitate is reflected in the time that the mixture takes to pass through the precipitate layer on the filter paper. The time taken to filter nominally 100g of the liquid varied and was not related to the quantity of precipitate produced. With the exception of Run 13 which appears to be a rogue result, there is a boundary below which filtration times are of the order of a few minutes and above which filtration rates are much greater. Some precipitates, Runs 6, 8 and 17 blocked the flow completely leaving a quantity of unfiltered material in the filter body. Results for these runs are excluded. For a three component mixture and saturates levels between 2.5% and 20% then this boundary is defined as:-

$$\% \text{ Pitch} = 0.43 \times \% \text{ saturates} + 19. \quad - (1)$$

If the pitch level in a mixture is less than the value calculated from its saturate content in equation (1), then the precipitate produced will offer only minimal resistance to flow. However, if the pitch level is greater than the calculated value, there will be increasing resistance to flow.

The boundary is shown in Figure 4. For a three component mixture with saturates levels below 2.5% there is minimal resistance to flow. The region within X, Y, Z is a hard brittle precipitate with high resistance to liquid flowing through it.

Mixtures of similar composition were filtered at 225°C, 250°C and 275°C. The results are shown in Table 2. The quantity of precipitate decreased with increasing temperature at a rate of approximately 1% absolute per 25°C rise above 200°C. It would be expected that if a triangular diagram similar to Figure 2, were to be drawn for the three component system at 275°C, there would be a greatly increased envelope in which precipitation would be insignificant and filtration times would also be reduced.

#### APPLICATION TO PROCESS CONDITIONS

Note: Triangular co-ordinates refer to (% Distillate Solvent, % Pitch, % Saturates).

##### Case 1

A typical LSE recycle solvent might contain 30% pitch and 10% saturates. If no saturates were present then the composition would be (70, 30, 0). As the saturates increase from 0 to 10%, the amount of precipitate produced rises to approximately 4% at 7% saturates (i.e. 63, 30, 7) and only a further 1% at 15% saturates (55, 30, 15). At this level resistance to flow could be experienced.

On occasions the solvent composition has reached (53, 40, 7) and blockages have occurred in the flow meter in the solvent feed line which is maintained at 150°C. As can be seen on Figure 4, this system would lie in the area where a hard, brittle and low permeability precipitate would form. Precipitation is eliminated at higher temperatures, however this would require replacement of trace heating and flow meters in the line and would increase the power consumption.

##### Case 2

Wash oil, which is comprised of distillate solvent and saturates only, is pumped along a line, approximately 20m long, to the base of the hydrocracker in order to continually flush the catalyst removal vessel. The line is narrow bore and the flow is 1 kg/hour at ambient temperature. If the flow in the line stops coal solution passes back down the line producing mixtures within a range of composition from wash oil (80, 0, 20) to coal solution (45, 50, 5) causing a precipitate to form. The precipitate will be hard and brittle in nature, Figure 4. Because there is no flow in the line, its surface temperature will increase and the precipitate will form insoluble carbonaceous material and consequently block the line. It was proposed LSE recycle solvent be used as flush oil giving a possible range of compositions in the line from (64, 30, 6) to (45, 50, 5). This avoids the area in which hard precipitate is formed. Further, solvent contains hydrogen donors which help to prevent the regressive reactions which cause coke formation. Since the switch from wash oil to solvent no problems have been experienced in this line.

##### Case 3

The bearings in the hydrocracker ebullating pumps are flushed with wash oil to both cool the pump bearings and protect it from coal solution. The wash oil re-enters the process steam at 100°C through an oil seal which has a 0.5 mm clearance. No solids can be tolerated in this oil as blockage of the oil seal would cause overheating and subsequent pump failure. Wash oil is chosen for this duty as the components are mutually soluble at these temperatures, no precipitate being present.

#### CONCLUSION

The mutual solubility characteristics of coal derived liquids can be determined using simple laboratory equipment and may be represented in terms of a three component system. Investigation of such systems have yielded results which have been applied to modify process conditions in a successful attempt to reduce costly interruptions to pilot plant operation.

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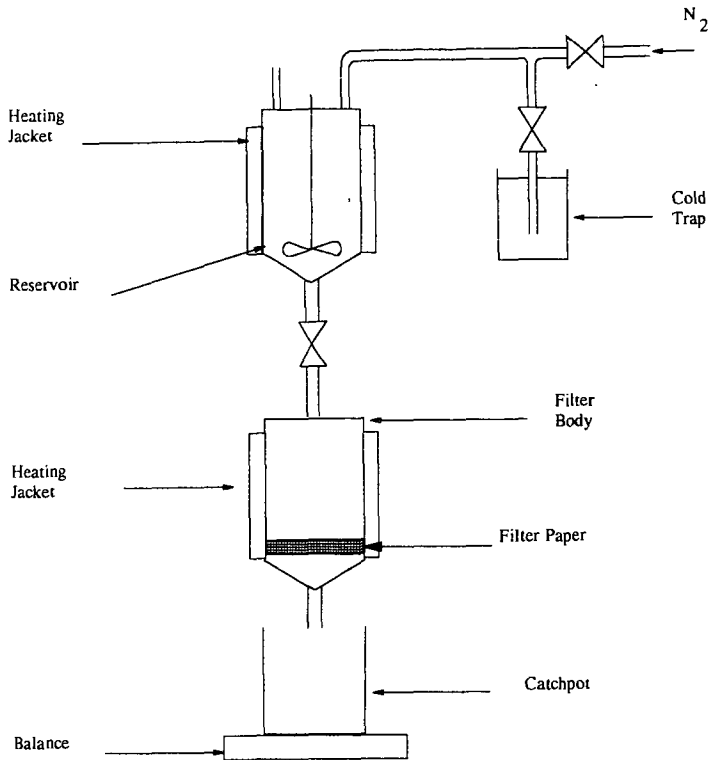
Table 1 - Quantity of Precipitate Produced for 3 Component Mixtures

Run Number	% Pitch	% Distillate Solvent	% Saturates	% Precipitate
1	21.4	60.1	18.5	6.0
2	20.4	60.8	18.8	4.8
3	11.9	65.0	23.1	4.1
4	25.1	57.6	17.3	5.4
5	33.4	55.0	11.6	4.9
6	36.4	50.4	13.1	7.7
7	36.8	60.3	2.9	1.3
8	22.7	68.5	8.8	12.0*
9	22.9	71.0	6.2	5.6
10	23.2	73.0	3.8	3.3
11	9.2	78.3	12.5	3.8
12	8.7	82.7	8.6	3.9
13	9.2	86.4	4.5	2.2
14	36.7	59.4	3.9	1.4
15	36.7	58.2	5.0	3.1
16	36.7	59.4	3.9	1.6
17	23.0	70.7	6.3	11.6*
18	9.4	82.1	8.4	3.5
19	3.1	92.5	4.4	1.0
20	6.0	89.9	4.1	1.8
21	14.9	70.4	14.7	5.4
22	17.7	78.1	4.2	3.3
23	4.7	81.0	14.2	2.0
24	11.3	79.6	9.1	3.8
25	35.0	58.0	7.0	5.9
26	25.4	61.9	12.7	4.3
27	15.3	69.2	15.6	4.5
28	20.9	59.3	19.7	8.2
29	31.8	53.9	14.3	4.4
30	38.8	50.1	11.1	4.2
31	10.1	65.5	24.4	2.2
32	16.7	62.0	21.3	4.2

Table 2 - Effect of Temperature on the Quantity of Precipitate Produced

Temp.	% Pitch	% Distillate Solution	% Saturates	% Precipitate	% QI	Filtrate Times (Mins.)	Mass Collected	Comments
225°C	23.4	68.0	8.5	3.0	11.4	2.5	58.1	Brittle Hard Precipitates
250°C	23.0	68.3	8.7	2.1	20.5	4.5	96.5	
275°C	27.2	68.1	8.7	1.2	46.6	1.2	95.7	

**Figure 1**  
**Laboratory Filter Rig**



**Figure 2**

Three component system Solvent / Pitch / Saturates at 200°C.

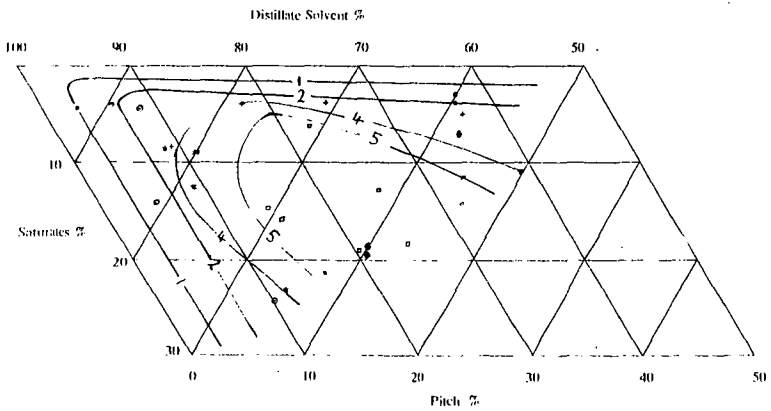


Figure 3

Composition of coal solutions for various pitch levels.

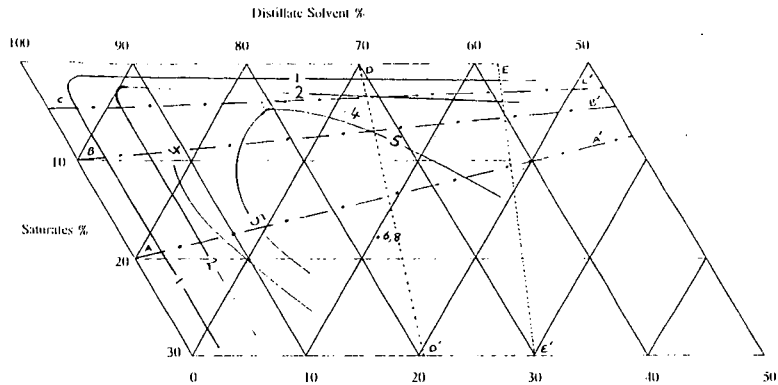


Figure 4

Titration times for the three component system at 200 °C

